# Raw Materials, Selection, Preparation and Characterization

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**Abstract** Among the different energy sources, biomass wastes hold most promise for the near future. Biomass is considered a neutral carbon fuel because the carbon dioxide released during its use is an integral part of the carbon cycle. Increasing the share of biomass in the energy supply contributes to diminishing the environmental impact of $CO_2$ and to meeting the targets established in the Kyoto Protocol. The use of biomass waste material as a fuel, however, has certain drawbacks related with its high-moisture content, low-energy density and the problem of reducing the size of the biomass, especially in the pulverized range of entrained flow gasifiers. Currently, there is increasing interest in developing new processes for the pre-treatment of biomass wastes, through the modification of their properties prior to gasification, so as to make them more attractive for their subsequent use. Pelletization is a proven technology for improving biomass properties, whereas torrefaction is considered a plausible alternative for decreasing the moisture content, increasing the energy density and greatly facilitating the handleability and grindability properties of the torrefied material.

## Notation

| | |
|---|---|
| CHE | Pellets from chestnut |
| BCOAL | Pellets from bituminous coal |
| COF | Pellets from coffee husks |
| GRA | Pellets from grape waste |
| HGI | Hardgrove Grindability Index |

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|---|---|
| PIN | Pellets from pine |
| RDF | Refuse derived fuel |
| TOP | Torrefaction and pelletization process |
| IGCC | Integrated gasification in combined cycle |

## 1 Introduction

The energy systems of most of the developed countries are based on fossil fuels at a time when the energy demand is continuously increasing. The limited reserves of such fuels are leading to a heavy dependence on imported fuels. If the amount of fuel needed to produce energy (rate energy/fuel) is reduced, more energy can be generated from the same amount of fuel, and the dependence on external energy supplies can therefore be reduced. Furthermore, the burning of fossil fuels produces pollutants and has a very negative impact on the environment, especially from the point of view of $CO_2$ emissions and climate change. For these reasons, one of the current challenges in energy production is to reduce the dependence on fossil fuels and to create a more sustainable scenario. One of the most promising approaches for diversifying energy resources is to resort to renewables, because these have a much less harmful environmental impact than fossil fuels and help to preserve the equilibrium of ecosystems. Moreover, renewable energies are indigenous resources and an increase in their use would have positive implications for the security of energy supplies. Among the different renewable energy resources available, biomass waste is the most promising for the immediate future as it is considered a carbon neutral fuel, i.e., the carbon dioxide released when biomass is used is an integral part of the carbon cycle.

Although several waste materials, such as biomass wastes, plastic wastes, used tyres and organic municipal solid wastes (RDF fraction), can be used directly as a solid fuel because of their high-heating value, their conversion into fuel gas or chemicals is an attractive alternative. Gasification can be considered as a way to recover energy from low-grade fuels, biomass, wastes or their mixtures [1, 2]. In particular, integrated gasification in combined cycle (IGCC) is highly efficient and has great potential for reducing the amount of man-made $CO_2$ emissions. Various solid fuels, including coal, biomass and wastes such as petroleum coke, heavy refinery residuals and municipal sewage sludge have all been employed as feedstocks in gasification systems [3–6].

However, the use of biomass waste material as a fuel entails several problems, including its high-bulk volume, high-moisture content and relatively low-calorific value, which make raw biomass an expensive fuel to transport. For biomass to produce an equivalent amount of energy as fossil fuels such as coal, very high loads of this material would be needed. Another drawback of some types of biomass (e.g., lignocellulosic materials) is that they are difficult to grind into fine particles. This problem is especially acute when biomass is to be used in pulverised systems, such as entrained flow gasifiers. All of these drawbacks have led to the development of new technologies, the aim of which is to improve the quality of biomass fuels so that they are easier to transport, process and handle.

This chapter mainly deals with new processes, such as torrefaction, that have been proposed as a means of treating biomass wastes to overcome some of the drawbacks of these renewable sources, in particular those related with densification, handleability and grindability. These problems are especially important when biomass is gasified with coal or petcoke, in entrained flow gasifiers where fine grinding is required, making the pre-treatment of the biomass particularly difficult when fibrous materials such as wood have to be handled.

## 2 Materials Pre-Treatment

The origin of biomass fuels can be very wide-ranging and they may be obtained from many sources, including forestry and agriculture residues, food-processing wastes or municipal and urban wastes. Likewise, the chemical constituents and moisture content of biomass materials are also extremely varied [7]. The characteristics of the biomass feedstock, especially moisture and mineral matter content, have a significant effect on the performance of the gasifier. The gasification of biomass that has a high-moisture content produces fuel gas with lower effective-heating values and higher tar concentrations. The energy valorization of these organic wastes requires as a first-step dewatering technologies with a low-energy consumption. Various types of pressure-assisted dewatering devices, such as filter presses, belt presses and centrifuges, can be used to reduce the water content. For many applications, mechanical dewatering cannot guarantee a sufficiently low-moisture content and, in this case, thermal drying must be used instead [8]. Many types of dryers are used to dry biomass, including direct- and indirect fired rotary dryers, conveyor dryers, cascade dryers, flash or pneumatic dryers, superheated steam dryers and microwave dryers. The direct flue gas biomass-drying technologies produce exhaust gases that contain high-volatile organic compounds [9]. The drying of biomass with superheated steam provides a more uniform drying over shorter periods at high temperatures. In modern drying technologies, woody biomass is dried in recirculated gas in conditions of relatively high humidity [10].

In moving bed gasifiers, the gas is made to pass through the biomass so the feed at the bottom has to have sufficient compressive strength to withstand the weight of the feed above it. In addition, the bed can tolerate only a limited amount of fines without experiencing an excessive pressure drop. In these gasifiers, particle sizes tend to be in the 20–80 mm range [11, 12]. Most biomass gasifiers use fluidized bed technologies, and bubbling beds are more common than circulating systems. In these gasifiers, the particle size is still in the millimetre range, and size reduction is not as critical as in the case of entrained flow gasifiers, where the short residence times make it necessary to pulverize the fuel [13].

## 2.1 Grindability

To prepare biomass for gasification, it is first necessary to reduce the material to a smaller size. However, it is usually not practical, nor necessary, to reduce the biomass feedstock to the same size as the coal feed. For biomass fuels, a wide range of equipment is used to produce different particle sizes. Grinding mills or hammer mills are used to produce particle sizes less than 5 mm, whereas particle sizes between 5 and 50 mm are produced by drum chippers and disc chippers, and the larger particle sizes (5–25 cm) by chunkers [14].

The dependence of most biomasses on seasonal availability and the higher efficiencies attained in larger coal gasifiers are among the causes that have led to the co-gasification of coal and biomass. There are, however, some disadvantages with this approach. In the case of entrained flow gasifiers where pulverized fuel is used, the addition of biomass quickly reduces the mill capacity during fuel handling because of the fibrous nature of some feedstocks. Higher throughputs can be achieved with dedicated co-use schemes. Nevertheless, co-milling is an attractive option compared with the alternative of a separate biomass feed system acting in parallel with the coal feed system as it avoids additional maintenance and installation costs [15].

An evaluation of the grinding behaviour of blends of biomass and solid fossil fuels (coal/petcoke) was conducted at the Instituto Nacional del Carbón (CSIC), as part of a Spanish project [16] coordinated by ELCOGAS, S.A., an electricity generating company that runs an IGCC of 335 MWe, using coal and petcoke as feedstocks. One of the objectives of this project was to select the most convenient biomass for co-gasification with a 50:50 blend of coal and petcoke. A mortar and pestle was used to grind the blends to which up to 20% of biomass was added and the particle size distribution of the different blends was determined.

Three biomass samples were used: (i) almond shells, (ii) olive oil waste and (iii) olive stones. The particle size distribution of the biomasses and the 50:50 petcoke–coal blend (CP–PT) are represented in Fig. 1. It can be seen that the coal–petcoke blend produces the highest amount of fines and does not contain any material greater than 212 μm under the conditions of the study. The results achieved for the biomass samples are clearly worse than for the coal–petcoke blend, with olive oil waste showing the best behaviour, as reflected by the higher amount of fine material in the <75 μm fraction. The olive stones also have a relatively high percentage of <75 μm particles.

Regarding the grinding behaviour of blends of 50:50 CP–PT with different percentages of biomass, the performances in the case of the almond shells and olive stones were similar. The addition of low amounts of biomass to the coal–petcoke blend increased the amount of large particles in the ground material. The behaviour of olive oil waste was different to that of the other biomasses, as can be seen in Fig. 2. For percentages of biomass of up to 10%, the grinding behaviour of the ternary blend was not affected and the particle size distribution of the blend was similar to that of the original coal–petcoke blend. However, when the

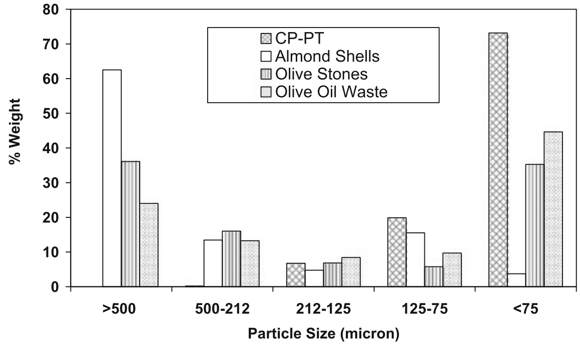

**Fig. 1** Particle size distribution of samples ground in a mortar and pestle

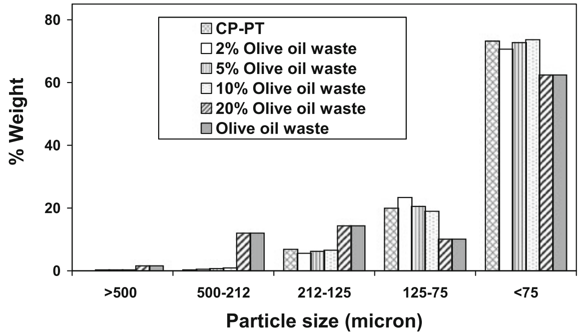

**Fig. 2** Particle size distribution of the ternary blend coal–petcoke–olive oil waste ground in a mortar and pestle

percentage of olive oil waste was increased to 20%, a notable increase in the number of larger particles was observed in the milled product in comparison with the coal–petcoke blend, 7% of the particles exceeding 125 μm in the case of this particular blend, whereas after the addition of 20% of olive oil waste, the percentage of particles greater than 125 μm raised to 26%.

## 3 Raw Materials Characterization

The characterization of fuels normally includes the proximate and ultimate analyses, and the calorific value, which give an indication of the quality of the fuel and its suitability. Because of increasing environmental constraints, analysis of metals concentration is also becoming more common. There are, of course, other properties that could be included in a more exhaustive fuel characterization, such as the ash fusion temperatures, the fuel particles hardness as measured by the Hardgrove grindability index and fuel density.

The nature and behaviour of the mineral constituents have a significant bearing on the design, operation and performance of the gasifier. For the gasification

**Table 1** Proximate and ultimate analyses and high-heating value of various samples

| Sample | Proximate analysis (wt.%, dry basis) | | | Ultimate analysis (wt.%, dry basis) | | | | | High-heating value (MJ/kg) |
|---|---|---|---|---|---|---|---|---|---|
| | Ash | Volatile matter | Fixed carbon | C | H | N | S | O | |
| Pine | 0.2 | 86.3 | 13.5 | 45.2 | 6.3 | 0.1 | 0 | 48.2 | 20.0 |
| Chestnut | 0.4 | 82.1 | 17.5 | 45.5 | 5.7 | 0.2 | 0 | 48.2 | 19.1 |
| Eucalyptus | 0.5 | 84.6 | 14.9 | 46.8 | 6.1 | 0.1 | 0 | 46.5 | 19.5 |
| Cellulose residue | 1.3 | 87.7 | 11.0 | 41.0 | 6.4 | 0.3 | 0 | 51.0 | 17.6 |
| Coffee husks | 4.5 | 79.4 | 16.1 | 43.2 | 6.3 | 2.6 | 0.2 | 43.2 | 20.1 |
| Grape waste | 7.5 | 67.9 | 24.6 | 50.0 | 6.0 | 2.0 | 0.1 | 34.4 | 22.1 |
| Almond shells | 1.2 | 79.3 | 19.5 | 49.2 | 6.0 | 0.2 | 0 | 43.4 | 19.7 |
| Olive stones | 0.6 | 81.4 | 18.0 | 50.6 | 6.1 | 0.1 | 0 | 42.6 | 19.0 |
| Olive oil waste | 7.1 | 77.3 | 15.7 | 48.9 | 6.2 | 1.4 | 0.2 | 36.2 | 21.6 |
| Petcoke | 0.6 | 12.6 | 86.8 | 87.2 | 4.1 | 1.5 | 5.4 | 1.2 | 35.2 |
| High-volatile bituminous coal | 7.6 | 37.7 | 54.7 | 77.9 | 5.1 | 1.7 | 1.5 | 6.2 | 32.4 |

process, the range of biomass materials and ash qualities, of which there is limited practical experience in real plant conditions, is a particularly acute problem in the case of entrained flow gasifiers. The proximate and ultimate analyses, and high-calorific value of selected waste materials, including a petcoke, are presented in Table 1. An analysis of a high-volatile bituminous coal is also provided for comparative purposes [17]. The ash contents of the majority of the biomass materials listed in Table 1, with the exception of the grape waste, coffee husks and olive oil waste, are quite low. In general, clean white wood materials have very low ash contents, generally less than 1%, whereas straw and grass materials, and the solid residues from the vegetable oil-producing industries, have ash contents in the 4–7% range.

The volatile matter content of the biomass materials is much higher than that of coal, ranging between 70 and 85%, as can be seen in Table 1. High-volatiles content increases the production of tars in all gasification systems except entrained flow gasifiers, which produce tar-free syngas. Nonetheless in these reactors, biomass is blended in low percentages with coal and/or petcoke [18]. In addition, the heating values of biomass fuels are lower than that of coal, as can be seen in Table 1. One of the limitations of biomass materials is their relatively low volumetric heating value or energy density (MJ/m$^3$), which is about five times lower than that of coal. This gives rise to concomitant problems related to the need for a large volumetric flow of biomass, even when co-gasifying small percentages of biomass with coal [19].

The drawbacks of using biomass for co-gasification, such as the difficulty of grinding to low particle sizes and the low-energy density of biomass, have prompted the search for new processes and methods of preparing biomass for co-feeding. These include densification through pelletization and/or torrefaction.

# 4 Improvement of Biomass Quality

## *4.1 Pelletization*

The densification of biomass waste materials contributes to improving their behaviour as a fuel by increasing their homogeneity and allowing a wider range of lignocellulosic materials to be used as fuel [20]. Wood pellets are also easier to handle, transport and store because of their uniform size, high density and low-moisture content [21]. All over the world, wood pellet markets are experiencing exponential growth. In fact, several new pellet plants are planning to base their production on more secure and cheaper feedstocks than sawdust. Increasingly, market parties, especially large-scale users, are experimenting with pellets made of straw, coffee husks, wheat husks and other agricultural residues [22].

The use of blends of coal and biomass could produce fuel pellets with more suitable characteristics for use in industrial furnaces, because coal has a higher carbon content and calorific value than biomass [7]. Apart from their increased density, and higher homogeneity, the quality of the pellets can be evaluated by measuring their mechanical resistance. This is quantified by means of the abrasion index, $I_a$, lower values of $I_a$ indicating a better pellet quality or a higher resistance [17].

The results of the abrasion index, $I_a$, for the pellets obtained from some of the raw materials presented in Table 1 are given in Fig. 3. The highest mechanical durability was attained with pellets from chestnut, CHE, followed by pine, PIN, and bituminous coal, BCOAL, whereas the pellets obtained from coffee husks, COF, and grape waste, GRA, were the weakest. Blending materials with high- and low-abrasion index have also been tried in an attempt to increase the mechanical resistance of some common wastes. The results of the work of Gil et al. [17] indicated that a blend of pine sawdust or chestnut sawdust with different percentages of a bituminous coal of up to 20% would be the most suitable for pellet production. In addition, a blend of this coal with eucalyptus sawdust was found to improve the mechanical durability of eucalyptus pellets considerably when the coal was added in a percentage equal to, or higher than, 10%.

As pointed out above, wood-based pellets are produced commercially around the world but there is only a limited production of agricultural biomass-based pellets. A recent study has developed a data-intensive techno-economic model for assessing the economic viability of using agricultural residue for pellet production [23]. The conclusions of this study indicate that for average and maximum yields, the cost curves are quite flat for a number of plants that produce 70,000 tonnes a year. This implies that plants smaller than the economically optimum size can be built with only a minor penalty cost. In addition, from a sensitivity analysis conducted in the same study, it was concluded that the total cost of pellet production is most sensitive to the field cost (cost of harvesting and collection, on-farm storage, nutrient replacement and farmer's premium) followed by the transportation cost.

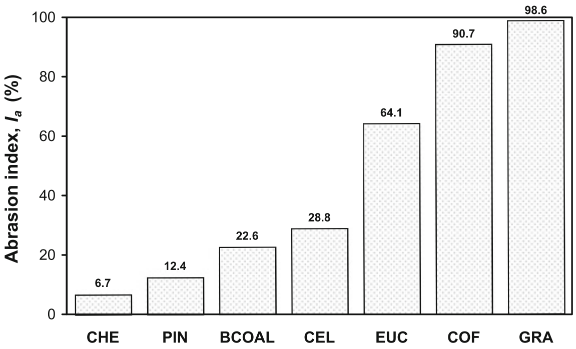

**Fig. 3** Abrasion index of pellets from different materials (cf. Table 1)

## 4.2 Torrefaction

The drawbacks of raw biomass waste, which include a low-energy density (typically 18 MJ/kg) and high-moisture content (around 10% even after drying), make the transport of biomass relatively expensive. A drying step would be insufficient as the biomass may regain moisture and result in storage problems, such as degradation and self-heating. Increasing the energy density of biomass is, therefore, seen as a necessary step to make biomass more useful and attractive as an energy source. On the other hand, it has been shown that higher gasification efficiencies can be achieved for fuels with low O/C ratios, such as coal, than for fuels with high O/C ratios, such as wood. Therefore, rather than gasify these fuels directly, it would seem preferable to modify their properties before gasification [24].

Torrefaction is a pre-treatment technology that makes biomass more suitable for combustion or gasification applications by addressing problems such as high-bulk volume, high-moisture content and poor grindability. The improved grindability of biomass after torrefaction may lead to higher use rates in the near future. Torrefaction is performed under atmospheric pressure at a relatively low-heating rate of less than 50°C/min in the absence of oxygen. Temperatures vary from 200 to 300°C according to the type of biomass. The biomass is partly decomposed and yields a solid product with a very low-moisture content and a high-calorific value, in addition to a condensable liquid and non-condensable gases. The main advantages of torrefied biomass include the production of a hydrophobic solid with a higher calorific value than that of the raw biomass, and the enhancement of grindability, because the energy consumption for milling is reduced by three to seven times with respect to the parent biomass [25].

Biomass is completely dried during torrefaction and after torrefaction the uptake of moisture varies from 1 to 6%. The hydrophobic nature of biomass after torrefaction can be explained by the destruction of OH groups, and the subsequent impossibility of hydrogen bonding. In addition, unsaturated structures are formed which are non-polar. This property is also the main reason why torrefied biomass is almost completely preserved and why biological degradation, as often observed with untreated biomass, does not occur anymore [26]. Torrefaction removes moisture and low weight organic volatile components and depolymerizes the long polysaccharide chains, producing a hydrophobic solid product with an increased energy density (on a mass basis) and greatly increased grindability. As a result, a significantly lower amount of energy is required to process the torrefied fuel and it no longer requires separate handling facilities when it is co-used with coal in existing power stations [15].

It has been stated that applying torrefaction as a biomass pre-treatment process can be expected to contribute to the technical and economic feasibility of entrained-flow gasification of biomass using existing feeding technology. Moreover, particles can be produced that are pneumatically transportable, which would be impossible in a bed of untreated biomass particles [26].

The changes in the grindability characteristics of biomass samples subjected to mild pyrolysis treatment or torrefaction has been studied in considerable depth by several authors. Bridgeman et al. [15] conducted an experimental research on the pulverization behaviour of two torrefied energy crops, willow and Miscanthus. The untreated and torrefied fuels were subjected to standard fuel analysis techniques, including ultimate analysis, proximate analysis and calorific value determination. The grindability of these fuels was then determined using a laboratory ball mill and by adapting the Hardgrove Grindability Index (HGI) test for hard coals. As the temperature and residence time of the process increased, a trend of decreasing volatile matter content was observed. The energy content of the torrefied biomass experienced an increase, the lowest energy yield (76%) corresponding to Miscanthus, at a treatment temperature of 290°C and a residence time of 1 h. The conclusions of the study showed temperature to be the most important parameter in terms of mass loss, increase in energy content, and ease in grindability of the solid product. It was also demonstrated that residence time plays an important role in facilitating grindability. The results demonstrated that Miscanthus was easier to pulverize than willow, the particle size distribution profiles of the pulverized pre-treated Miscanthus being similar to those of coals with similar or equivalent HGI values. The authors also concluded that particle size distribution is a more satisfactory method of analysis of grinding behaviour than the modified Hardgrove Grindability Index used in their work.

Arias et al. [27] evaluated the influence of torrefaction on the grindability of eucalyptus. 10–15 g of biomass was ground and sieved to a particle size of 5 mm. Torrefaction was performed under a nitrogen atmosphere, at a heating rate of 10°C/min up to three different final temperatures (240, 260, 280°C). The samples were kept at the final temperature for different residence times (0 to 3 h). Torrefaction increased the gross calorific value with the temperature treatment and the residence time. In the most critical conditions studied in their work (280°C and 3 h), the gross calorific value of the product increased by 34% with respect to that of the raw biomass. However, during torrefaction, there was a loss of energy with respect to the original biomass, as was computed from the heating value yield. Figure 4 shows the evolution of the heating value yield of the torrefied eucalyptus. Here the heating value yield ranges from 92% for the sample treated up to 240°C (TRE-0-240) to the unacceptable value of 67% for the sample treated at 280°C for

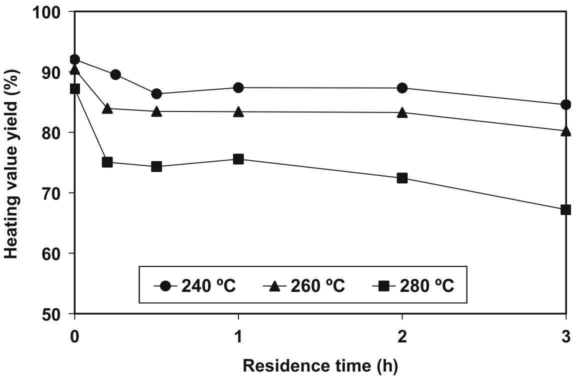

**Fig. 4** Variation in the heating value yield of torrefied eucalyptus for different treatment temperatures and residence times (reprinted from Arias et al. [27] with permission from Elsevier)

3 h (TRE-3–280). It can be seen from the results in this figure that even at low residence times, treatment at 280°C produces a large decrease in the heating value yield. For the other two temperatures (240 and 260°C) the heating value yield remained practically constant from 30 min to 2 h of treatment, with a slight reduction being observed after 3 h.

The grindability characteristics of the torrefied eucalyptus were evaluated by treating the samples in a cutting mill and sieving the samples into four size fractions. The particle size distributions of the torrefied eucalyptus samples are shown in Table 2. In the case of the raw eucalyptus only 29% of the untreated biomass passed through the 425µm sieve. In all cases, there is an improvement in the grindability characteristics of the treated biomass, the percentage of particles passing to the lower size fractions greatly increasing for the samples subjected to torrefaction. The results of the work of Arias et al. [27] indicated that a mild torrefaction treatment at 240°C for 30 min could improve the grinding characteristics of the biomass with little loss of heating value yield.

A combination of the processes of pelletization and torrefaction has been developed at the Energy Research Centre of the Netherlands (ECN), and has been named as the TOP process [28]. Densification by means of pelletization is considered to be a proven technology for improving the properties of biomass for its conversion into heat and power. However, biopellets are expensive, require special treatment at the power station and can only be produced from a limited variety of biomass feedstock. The TOP process integrates the advantages of torrefaction and pelletization with respect to the quality of the biopellet. The experimental work conducted at ECN revealed that TOP pellets may have a bulk density of 750–850 kg/m$^3$ and a net calorific value of 19–22 MJ/kg as received. This results in an energy density of 14–18.5 GJ/m$^3$, which is reasonably similar to that of subbituminous coal (16–17 GJ/m$^3$). The energy density is significantly higher than that of conventional biopellets produced from softwood (sawdust: 7.8–10.5 GJ/m$^3$). In contrast to conventional biopellets, the TOP pellets can be produced from a wide variety of feedstock (sawdust, willow, larch, verge grass, demolition wood and straw) yielding similar physical properties.

**Table 2** Particle size distribution of torrefied eucalyptus

| Sample | >425 μm | 425–150 μm | 150–75 μm | <75 μm |
|---|---|---|---|---|
| RE | 71.2 | 18.7 | 4.7 | 5.4 |
| TRE-0–240 | 55.5 | 32.1 | 8.8 | 3.6 |
| TRE-0.5–240 | 43.2 | 36.3 | 13.1 | 7.4 |
| TRE-1–240 | 51.9 | 29.9 | 12.2 | 6.0 |
| TRE-3–240 | 39.7 | 35.4 | 12.5 | 12.4 |
| TRE-0–260 | 46.8 | 34.1 | 12.3 | 6.8 |
| TRE-0.5-260 | 37.9 | 34.6 | 13.5 | 14.0 |
| TRE-1–260 | 44.1 | 37.9 | 13.3 | 4.7 |
| TRE-3–260 | 35.5 | 35.8 | 18.1 | 10.6 |
| TRE-0–280 | 45.6 | 36.7 | 10.8 | 6.9 |
| TRE-0.5–280 | 36.2 | 35.6 | 12.7 | 15.5 |
| TRE-1–280 | 46.6 | 35.8 | 12.7 | 4.9 |
| TRE-3–280 | 33.9 | 37.0 | 18.8 | 10.3 |

## 5 Conclusions

The use of biomass waste materials for gasification is increasingly seen as a means of reducing the dependence on fossil fuels and reducing the emissions of $CO_2$ to the atmosphere. The disadvantages associated with the high-moisture content and the low grindability properties of biomass waste materials can be greatly reduced by applying new processes such as torrefaction or a process that combines pelletization and torrefaction. The reduction in the size of the biomass is an energy consuming process that subjects the equipment to excessive wear. The torrefaction of biomass decreases energy consumption, while increasing production capacity with respect to the untreated, raw material. The higher energy efficiencies achieved in pressurized entrained flow gasifiers would make the co-gasification of coal and/or petcoke with biomass wastes, and the pre-treatment of biomass (i.e., torrefaction) more attractive for the industrial application.

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